

ACTIVITY REPORT

April 2004



**Natural
Gas &
Oil
Technology
Partnership**

Bringing Department of Energy national laboratories capabilities to the petroleum industry.

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Note: Natural Gas and Oil Technology Partnership projects are reported according to the following schedule:

January, March, May, July, September, November
Drilling, Completion, and Stimulation Technology
Oil and Gas Recovery Technology
Diagnostic and Imaging Technology

February, April, June, August, October, December
Natural Gas Technology
Upstream Environmental Technology
Downstream Environmental Technology

Natural Gas and Oil Technology Partnership on the World Wide Web: <http://www.sandia.gov/ngotp/>

Upstream Environmental Technology

Estimation and Reduction of Air Quality Modeling Uncertainties

(Envair, EPRI, and LBNL)

This project is in "Inactive" status.

Remote Sensing for Environmental Baseline and Monitoring

(US Geological Survey (USGS), and USDA Agricultural Research Service (ARS), and ORNL)

Highlights:

- Completed high and low resolution geobotanical maps for nine sites.
- Correlating geobotanical maps to field data for the two USGS sites.

The US Geological Survey (USGS), the USDA Agricultural Research Service (ARS), and ORNL are collaborating to develop remote (airplane or satellite) hyperspectral sensor techniques to identify areas impacted by oil production. ORNL has completed the analysis of the hyperspectral images for nine sites in Osage County. The area of the Site B analysis region was expanded from 12,740 pixels to 90,720 pixels. The number of pixels ranges from 23,100 for Site A to 104,160 for Bluestem 134. Using two different cluster radii - 0.010 and 0.004 - high and low resolution clustering was performed. For the larger radius, the number of clusters ranges from 35 for Zink Ranch 127 to 133 for Bluestem 134. For the smaller radius, the number of clusters ranges from 100 for Site A to 418 for Bluestem 134. Both high and low-resolution geobotanical maps have been created.

To compare the geobotanical maps to field data, one-cluster maps have been prepared for all of the high and low resolution clusters for the two USGS sites. The preliminary analysis of cluster maps suggests that the salt scars and salt-affected soils at both the "A" and "B" sites produce distinctive cluster associations that differ from other disturbed areas, areas with poor vegetation because of shallow bedrock and thin sandy soils, and exposed lake bottom. However, there are no clusters that seem to uniquely occur on the salt-scarred areas. Cluster pixels that occur on the salt scar also occur in other areas of thin, sparse, or absent vegetation on rocky to sandy and clayey soils in other settings in the map scene.

Some clusters are very useful, for example, Cluster 69 in the Site B map (the 82 cluster version) appears to be linked to the occurrence of hydrous ferric oxide (HFO) at the disturbed soil surface. This signature occurs in the salt scars at Site B where reduced iron in shallow saline ground water comes to the surface forming seeps of iron-rich water that is oxidized and stains the surface sediment with HFO. However, it also occurs at disturbed sites, such as graded drill pads, where the sandy to bouldery colluvium exposed in cuts at the edge of the drill pad is also iron-stained. Cluster 66 in the Site B map (the 82 cluster version) is clearly linked to asphalt. It occurs over the asphalt road on the ridge crest but it also occurs over crude-stained soils at the west edge of the active pit at Site B.

In areas that were initially densely vegetated by oak forest, like the B Site as seen in 1936 aerial photography, the relatively simple bright pixel map provides a useful view of the extent of site disturbance due to oil-field activities. A quantitative measure of the total disturbed surface area of the scene could be obtained by pixel counting.

Modeling of Water-Soluble Organic Content of Produced Water

(ChevronTexaco, ConocoPhillips, Shell, Statoil, and ORNL)

The main thrust during the last two months has been to plan this year's work with an anticipated much reduced budget. Once funding arrives, the thermodynamic and statistical modeling efforts, which have been performed separately, will be combined into a single approach. The final model will be documented and the project completed.

Science-Based Methods to Assess Risks Attributable to Petroleum Residues Transferred from Soil to Vegetation

(ChevronTexaco, PERF UC-Berkeley, UC-Davis, and LBNL)

Highlights:

- Evaluate field data on plant uptake from PERF 97-06
- Presented chamber study results at SETAC conference

LBNL received and reviewed hydrocarbon uptake data from PERF Project 97-06 where ChevronTexaco is one of the participating companies. PERF 97-06 is titled "Phytoremediation of Hydrocarbons - Phase II Field Project" and the sponsor company is ExxonMobile. The data was provided through ChevronTexaco. The data included co-located measurements of polycyclic aromatic hydrocarbon (PAH) concentrations in soil and vegetation from a number of phytoremediation study sites. LBNL reviewed the data and provided initial comments to the contact person at PERF 97-06 and will continue to evaluate data for use in current study. Additional details on PERF 97-06 can be found at <http://www.perf.org>.

LBNL presented results from plant uptake experiments for PAHs and n-alkanes at the Society of Environmental Toxicology and Chemistry (SETAC) conference. Experimental work and sample analysis will resume when FY 2004 funding arrives.

Presentations:

R.L. Maddalena, T.E. McKone, R. Kobayashi and N.Y. Kado. "Controlled Measurements of the Multi-Pathway Uptake of PAHs and n-alkanes from Soil into Wheatgrass" SETAC Europe 14th Annual Meeting. Prague, Czech Republic, April 18-22.

Interactive Information System on Drilling Waste Management Practices

(ChevronTexaco, Marathon, and ANL)

Highlights:

- Project Paper well received; other presentations scheduled for 2004
- New Website nearing completion

A paper describing the project was presented last year at the SPE/EPA/DOE Exploration and Production Environmental Conference in San Antonio, TX. The presentation was well received by the audience. Future presentations are scheduled during the summer and fall of 2004.

We have received inquiries from around the world concerning the Website and when it will be publicly available. The full draft Website was finished at the end of March. The draft Website was distributed to an external government/industry review panel in early April. Comments are due back in early May. We hope to have a final, publically-available Website online by the summer of 2004.

Use of Ionic Liquids in Produced Water Clean Up

(ChevronTexaco, Shell, Conoco-Phillips, ORNL)

Highlight:

- Contact experiments, solubility of produced water organics in ionic liquids complete.

The series of tests involving contacts between aqueous phases with concentrations of organics typical of produced water and ionic liquids is complete. Nine separate ionic liquids were tested, with a variety of chemical and physical properties. Although some variation was observed, the ionic liquids had a high affinity for alcohols and aromatics, and less so for organic acids and ketones. Aliphatic hydrocarbons had even lower solubility in the ionic liquids being tested. Factors such as pH, temperature, salinity, and length of contact time were investigated, as was regeneration of the ionic liquid solvents. The results from these experiments are being analyzed and documented.

Downstream Environmental Technology

A Predictive Model of Indoor Concentrations of Outdoor PM_{2.5} in Homes

(Aerosol Dynamics, Western States Petroleum Association, and LBNL)

In the LBNL study to understand the relationship between indoor and outdoor concentrations, the chemical components of PM_{2.5} for a well-characterized, unoccupied residence, time-resolved, indoor and outdoor measurements of particle size distributions and chemical composition have been made to elucidate mechanisms of particle penetration, deposition and phase transformations. These analyses have specifically addressed the dynamic nature of indoor/outdoor concentration relationships and how the time-dependence of outdoor concentrations influence indoor concentrations.

A related question is how well the concentrations measured inside the Clovis study home could be predicted on the basis of measurements at the central monitoring site, located 6 km distant. To answer this question, we are examining the variability between the airborne concentrations of PM_{2.5} nitrate, sulfate and black carbon measured immediately outside the study house to that determined at the central monitoring station located 5 km to the southwest. The data set at both sites includes 20-minute averaged sulfate and nitrate data collected with the integrated collection and vaporization system, and the 20-minute black carbon data determined by aethalometer. The question we are addressing is whether the differences between outside the house and the central monitoring site are of significance for predicting the distribution of indoor concentrations using 20-minute averaged data from the continuous monitors.

Comparison is made between the "Central Station" and "Outdoor" measurements for the period of October 2000. As expected, data are most highly correlated for sulfate ($R=0.91$), which is a stable, secondary component and regional in extent, and are lowest for black carbon ($R=0.74$), which is affected by local sources. The correlations increase slightly when the outdoor Clovis data are compared to the measurements made 20 minutes earlier at the Fresno Central Site for the secondary components, nitrate and sulfate. Using a linear fit to the data between the two monitoring locations, taking into account the 20-minute offset for sulfate and nitrate, we compare the outdoor concentration estimated from the central site data to those which were observed. For sulfate, the pooled standard deviation between the estimated and observed value was $0.6\mu\text{g}/\text{m}^3$, or 19% of the mean value. Corre-

sponding values comparing estimated and measured outdoor nitrate are $4.5\mu\text{g}/\text{m}^3$ or 36% of the mean nitrate concentration. For black carbon the standard error in the estimated outdoor black carbon was $0.6\mu\text{g}/\text{m}^3$ or 48% of the mean value. When comparisons are made on a four-hour basis, the outdoor concentrations estimated from the central site monitoring data are closer to the measured outdoor value, yielding pooled standard deviations between estimated and measured value of 11%, 25%, and 29% for sulfate, nitrate and black carbon, respectively. While longer time averages yield closer comparisons, the time variability has been shown to be important to the estimates of indoor concentrations. Of interest is how errors in the assumed outdoor concentration value propagate when estimating the distribution of indoor concentrations. For nitrate, indoor concentrations depend on other factors such as the indoor temperatures and the indoor removal of nitric acid and thus uncertainties in the outdoor nitrate may not be as important as for a stable component such as black carbon. These issues are currently being addressed.

Technology Transfer:

An abstract has been submitted for presentations at the 2004 Fall Meeting of the American Association of Aerosol Research to be held in Atlanta Georgia:

"The Transport and Fate of Outdoor Carbonaceous Aerosols in the Indoor Environment," by Melissa M. Lunden, Thomas W. Kirchstetter, Tracy L. Thatcher, and Nancy J. Brown, Lawrence Berkeley National Laboratory, 1 Cyclotron Rd., Berkeley, CA 94720; Susanne V. Herring, Aerosol Dynamics, 2329 4th Street, Berkeley, CA 94710.

A Predictive Model of Indoor Concentrations of Outdoor Volatile Organic Compounds in Homes

(American Petroleum Institute, Western States Petroleum Association, and LBNL)

Substantial progress was achieved on method development and a pilot field study to quantify material surface areas available for sorption in real residential environments. This work was performed primarily by Katherine Ming, a student in the DOE's Office of Science Undergraduate Laboratory Internship (SULI) program under the supervision of Dr. Brett Singer. A methodology was developed to efficiently measure large material surface areas and estimate smaller material surface areas in occupied residential settings. A database was constructed in Microsoft Access to facilitate the recording of materials and areas by room and location. The database can also be used to determine total surface area by material and by room within each dwelling. To initially populate the database, a pilot survey of three dwellings was performed. They included a dormitory room and three occupied houses in Berkeley and Oakland, CA. The documented methodology can be used to conduct surveys of additional homes to expand the database. The database will be used to evaluate the relevance of various furnishing scenarios employed for sorption experiments in LBNL's 50-m^3 room-sized environmental chamber and to provide values of material surface areas to use in modeling of "typical" residential scenarios. We have previously determined that, outside of ventilation, sorption is likely to be the most important process affecting indoor exposures to volatile organic hazardous air pollutants (HAPs) entering from outdoors. Variability in materials and surface areas among residences is likely to result in variations

in sorption that will affect exposures. Estimating these variations is an important task for this project.

Technology Transfer:

The citation for the published paper that describes our earlier work on this project is:

Singer, B.C., K.L. Revzan, T. Hotchi, A.T. Hodgson, and N.J. Brown, "Sorption of Organic Gases in a Furnished Room," Atmospheric Environment, V38, N16: 2483-2494, 2004.

Characterization and Reaction Behavior of Sterically-Hindered Sulfur Compounds in Heavy Crudes with Nano-Sized Molybdenum Disulfide

(ChevronTexaco, BNL, and ANL)

Project suspended pending renewed funding.

Development of a Solid Catalyst Alkylation Process Using Supercritical Fluid Regeneration

(Marathon-Ashland and INEEL)

Project suspended pending renewed funding.

Secondary Organic Aerosol Research in the Sierra Nevada Foothills

(Aerosol Dynamics, Independent Petroleum Association of Mountain States, and LBNL)

Recent efforts have focused on characterizing the particle growth events that are observed in the forest during the 2002 field measurement season. The data have been aggregated over a number of different time frames - from weeks to months and seasons - to discern the diurnal patterns in the different particle, meteorological, and gas phase data. Comparisons between these calculations have shown that total particle concentration correlates strongly with ozone, implying that these particles are formed by oxidation processes. The data also show that black carbon concentration, a signal of anthropogenic emissions, tend to increase approximately four hours after the increase in particle concentration, implying that the formation processes that occur before this are likely strongly influenced by local emissions. A routine that fits the measured aerosol size distributions has been developed to provide data regarding the change in the characteristics of the distribution as a function of time. The results of the fit provide information such as the change in the geometric mean particle size as a function of time. We calculate changes in particle mass as a function of time and particle size from the fits that can be linked to gas phase data to discern probable growth mechanisms. A manuscript detailing our observations regarding the particle growth events is being prepared.

We continue to observe how distant forest fires in California and Oregon affect pollutant concentrations at the Blodgett field location. During times that appear to be affected by forest fire emissions (as evidenced by enhanced black carbon emissions and the presence of a larger mode in the size distribution), the ozone concentrations and specific biogenic species concentrations appear to be enhanced. We are collaborating with investigators from Colorado State University who are conducting another study designed specifically to determine the effect of forest fires on visibility at Yosemite National Forest. A comparison between the data collected at Yosemite and Blodgett shows strong correlations between black carbon data during the height of the "Biscuit" fire

in southern Oregon last August. This results shows that forest fires emissions can be transported long distances, and impact air quality and visibility over large areas.

Technology Transfer:

Two abstracts have been submitted for presentations at the 2004 Fall Meeting of the American Association of Aerosol Research to be held in Atlanta Georgia:

1) Melissa M. Lunden, Douglas R. Black and Nancy J. Brown, Lawrence Berkeley National Laboratory; Anita Lee, Gunnar W. Schade and Allen H. Goldstein, Division of Ecosystem Sciences, Department of Environmental Science, Policy, and Management, University of California, Berkeley, CA 94720. "Correlations Between Biogenic Volatile Organic Compounds, Anthropogenic Pollutants, and Aerosol Formation in a Sierra Nevada Pine Forest," April 2004.

2) Melissa Lunden, Douglas Black, Nancy Brown, Lawrence Berkeley National Laboratory; Gavin McMeeking, Sonia Kreidenweis, Christian Carrico, Taehyoung Lee, Jacqueline Carrillo, and Jeffrey Collett, Jr., Department of Atmospheric Science, Colorado State University; Derek E. Day, Jennifer L. Hand and William C. Malm, CIRA, Colorado State University. "The Influence of Forest Fires in the Western United States on Pollutant Concentrations in California During the Summer of 2002," April, 2004.

Proton Exchange Reactive Membranes for Conversion of Light Alkanes to Clean Liquid Fuel

(Ceramatec, Inc. and INEEL)

Project suspended pending renewed funding.

Bioupgarding of Heavy Crudes Using Temperature and Oil Tolerant Enzyme Catalysts

(ChevronTexaco and ORNL)

Highlight:

- Produced P450 enzymes for substrate binding studies.

Project description: This project is aimed at developing catalysts that can be used at temperatures up to 90°C and in an oil environment with the goal of upgrading crudes via oxidative biotransformation or molecular weight reduction. Cytochrome P450 enzymes capable of oxidation of various polycyclic aromatic hydrocarbons (PAH) and alkanes are being used for developing improved biocatalysts.

Progress: The P450 enzymes CYP 119 and hybrid P450 reported previously were produced in 5L cultures. The two enzymes were purified using a two-step purification protocol using an ion exchange HTQ column (Amersham Biosciences) and a polybuffer exchange chromatofocussing column. The purity of both enzymes was more than 95% based on UV-vis Spectra. The enzymes are being studied for binding characteristics using various hydrocarbon substrates. This will be the last experiment to be conducted on this project. A final report will be submitted subsequently.

Natural Gas Technology

Molecular Engineering: Next Generation of Gas Purification Technology

(ChevronTexaco, Virginia Commonwealth U, and BNL)

The objective of this project is to develop a gas filtration technology based on a molecularly imprinted polymer (MIP) in which a gas template is imprinted on a polymer thin film to selectively and efficiently separate target gases to upgrade natural gas from gas fields.

The imprinted polymeric materials are being synthesized using rapid precipitation from a supercritical solution followed by vapor treatment and UV photo polymerization. The process produces a material with pore size tuned to the template vapor but without chemical functionality. The RESS (Rapid Expansion of Supercritical Solution) method of MIP preparation has been successfully demonstrated for heptane template. The RESS process was applied to prepare three nanocoatings of the polymeric material derived from the 2,5-distyrylpyrazine (DSP) monomer. The nanocoatings were prepared on glass slides to screen their suitability for X-ray diffraction (XRD). The XRD data of two DSP samples of varying thickness and one pure crystalline DSP sample are being analyzed. A procedure is being developed to produce nanocoatings directly on the XRD capillary tubes. The goal is to produce and optimize nano-scale uniform particulate coatings.

Work is now continuing to further reduce the molecular porosity of the imprinted materials for efficient separation of small molecules such as N_2 , CO_2 , and H_2S from CH_4 . Work continues preparing MIP samples that are suitable for XRD analysis. The Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), porosity, and XRD measurements on the prepared samples continue. A laboratory-scale unit is being designed to demonstrate gas purification efficiency of the MIP based system as set forth in the objectives.

Coiled-Tubing-Deployed Hard Rock Thermal Spallation Drill and Cavity Maker

(Nextant, NM Tech, and LANL)

Highlight:

- Burner successfully operated at the design propane flow rate.

Design Review: Los Alamos and NM Tech reviewed their current burner design and prepared for a final design of the connector sub that will be used to attach the NM Tech burner to the coiled tubing.

Down Hole Ignition: Los Alamos is evaluating off-the-shelf flame ignition components to determine if a downhole igniter can be configured in the burner and connector sub to ignite the burner in the drill hole. Several spark plugs have been evaluated and a piezoelectric propane igniter has been procured for evaluation. Evaluation results with the spark plugs to date have not been encouraging.

Coiled Tubing Procurement: Los Alamos tested the conductors in the telemetry cable that are installed inside the coiled tubing that was procured to demonstrate spallation. All eight conductors' demonstrated continuity and seven of the conductors had high impedance between the conductor and the stainless tubings that were installed inside the coiled tubing.

Ten Foot Spallation Test Attempt: NM Tech operated the field burner on the spallation drilling platform at 110% the design flow rate using the large burner exit nozzle that produces subsonic flow of the exhaust. The demonstration followed a number of attempts which failed to achieve

even 70% of the designed flow rate. The 110% flow was achieved after a complete disassembly, cleaning, and reassembly of the burner. They believe that fouling of the tiny propane apertures in the mixing nozzle has been limiting the burner performance. Cleaning of the apertures has proven to be difficult.

NM Tech has not been able to ignite the prototype nor the field burner when a small nozzle is installed in the burner outlet. The small nozzle is sized to produce a mach 1.5 exhaust velocity. Neither the Los Alamos design review nor the continuing NM Tech investigation have identified any reason that the small nozzle precludes ignition of the burner.

Scintillating Fiber Neutron Detectors for Well Logging

(CompuLog, Precision Drilling, Technology Services Group, and PNNL)

Highlight:

- Additional funding recieved

The work continues to focus on electronics. Amplifier performance evaluations are underway. High temperature electronics options are being investigated. New electronics staff were brought on to the project. The location for preliminary neutron response testing is being relocated to a lower background area. High temperature epoxy compatability experiments are underway. Additional funds were released to the project which will accelerate progress. A summer student in nuclear engineering will assist in detector testing.

225° C MWD Using Silicon-On-Insulator (SOI) Electronics

(Baker Oil Tools, Eagle-Picher, Honeywell SSEC, General Atomics, Noble Engineering, Quartzdyne, and SNL)

Project suspended pending renewed funding.

Partnership Office

Due to budget constraints, no new-start projects were solicited for fiscal year 2004.